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A Transferable Intermolecular Potential for Nitramine Crystals

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A Transferable Intermolecular Potential for Nitramine Crystals

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Abstract

We have analyzed the transferability of a previously proposed Buckingham repulsion-dispersion intermolecular potential for the explosive hexahydro-1,3,5-trinitro-1,3,5-s-triazine (RDX) (Sorescu, D. C., B. M. Rice, and D. L. Thompson, *Journal of Physical Chemistry B*, vol. 101, p. 798, 1997) to predict the crystal structures (within the approximation of rigid molecules) of a database of 30 nitramines. These include acyclic, monocyclic, and polycyclic molecules. It is shown that the proposed potential model is able to accurately reproduce the crystallographic structures and lattice energies (where available) of these crystals. For the majority of these crystals, the best agreement with experimental structural and energetic data is obtained in those cases when the electrostatic charges have been determined using *ab initio* methods that include electron correlations effects (namely MP2 and B3LYP). The use of the electrostatic charges calculated at the Hartree-Fock level results in large deviations of the predicted lattice energies from the experimental values. The deviations of the lattice energies can be significantly decreased by scaling the electrostatic charges with a constant factor.

Acknowledgments

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1. Introduction

Atomistic simulation is increasingly gaining acceptance as a practical research tool in the investigation of the behavior of condensed-phase materials. In addition to providing information that is difficult or impossible to measure, prediction leads to a reduction in unnecessary measurement or synthesis of candidates in the course of design of new materials. However, the power of atomistic simulation can only be realized if the description of the molecular system is accurate. The development of accurate intermolecular potentials is not a simple, straightforward procedure. Substantial work has been directed toward determining both simple functions that make large-scale simulation realizable, and correct parameterization such that the physical properties of the materials are properly described. In this work, an intermolecular potential that accurately describes nitramine crystals is presented. Also, the potential parameters effect on predictive ability is investigated.

In initial studies of nonreactive processes in the nitramine explosive hexahydro-1,3,5,-trintro-1,3,5-*s*-triazine (RDX), an intermolecular potential energy function was developed that would accurately reproduce the structure of the α-form of the RDX crystal [1]. This potential is composed of pairwise atom—atom (6-exp) Buckingham terms with explicit inclusion of the electrostatic interactions between the charges associated with the atoms of different molecules. The parametrization of the potential function was done such that molecular packing calculations (MP) reproduced the experimental structure of the crystal and its lattice energy. Isothermal-isobaric molecular dynamics simulations (NPT-MD) using this potential energy function predicted crystal structures in excellent agreement with the experimental data [1].

It has been shown that this interaction potential energy function is transferable to two other nitramine crystals: the polycyclic nitramine 2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (HNIW) [2] and the monocyclic nitramine 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) [3]. Both MP and NPT-MD simulations predict geometrical parameters in good agreement with the experimental values for the different polymorphs of the HNIW and HMX crystals [2, 3].

Furthermore, the calculations indicate a stability ranking for HNIW in agreement with experimental measurements [4].

The success of these potential energy parameters in describing the RDX crystal and different phases of the HMX and HNIW crystals provides impetus for further investigations to determine the limits of the transferability of this interaction potential. Toward this end, MP calculations of 30 nitramine crystals are reported here. This set of crystals is composed of monocyclic, polycyclic, and acyclic nitramine molecules. There was a particular interest to see if the geometrical and energetic parameters for these crystals could be reproduced by this proposed model.

One of the main factors that contributes to the quantitative description of the molecular packing in a crystal is related to the representation of the electrostatic interactions. It was shown more than a decade ago [5, 6] that increased accuracy in structural predictions of the molecular crystals and in transferability of the potential parameters can be achieved by explicit use of the electrostatic interactions between the charges associated with the atoms. For example, many of the available force fields such as Amber [7], ECEPP [8], or Dreiding [9] use these kinds of potential terms in models of organic, biological, and main group inorganic crystals. Further improvement of the description of the electrostatic forces between molecules, particularly in crystals with substantial anisotropies, can be achieved by using sets of point multipoles (charge, dipole, quadrupole, etc.) on every atomic site. This distributed-multipole representation has been shown to be successful in the modeling of the crystal structures of polar and hydrogen-bonded molecules [10].

The present study has found that, as in the cases of the RDX [1], HNIW [2], and HMX [3] crystals, the set of 30 crystals considered here can be accurately represented using the Buckingham potential plus Coulombic interactions. The assignment of the electrostatic charges poses a problem in that the atom-centered monopole charge is not an observable quantity and cannot be obtained directly from either experiment or first principles calculations. Currently,

there are several schemes for evaluation of charges by empirical partition or by using a quantum mechanically derived wave function [11–13]. The Coulombic terms have been determined through fitting of partial charges centered on each atom of the molecules to a quantum mechanically derived electrostatic potential [13]. An investigation has been done on how the geometrical and energetic parameters predicted in MP calculations depend on charges determined from *ab initio* methods, which do or do not include electron correlation effects. Specifically, different sets of charges derived from the Hartree-Fock (HF) wave function [14] and from methods that employ electron correlations such as second-order Möller-Plesset (MP2) [15–18] and B3LYP [19, 20] have been used.

The studies described here represent the first stage in the development of a general model for nitramine crystals. The main limitations of the present model are due to the assumption of rigid molecules but further refinement of this model can be made to include the effects of intramolecular motions, particularly of low-frequency torsional motions of the nitro groups and the ring.

The organization of the paper is as follows. In section 2, the intermolecular potential used to simulate the nitramine crystals is presented. In sections 3 and 4, the molecular packing methods and results, respectively, are described. The main conclusions are summarized in section 5.

2. Intermolecular Potential

The central problem in classical simulations of molecular crystals is the construction of realistic potentials that accurately predict the structural and thermochemical parameters. In this paper, the same general model is employed for the atom-atom potentials that proved to be successful in modeling of the RDX, HNIW, and HMX crystals [1–3]. In particular, it is assumed that (1) the intermolecular interactions depend only on the interatomic distances; (2) the interaction potential can be separated in contributions identified as van der Waals and electrostatic, and (3) the same type of van der Waals potential is used for the same type of atoms,

independent of their valence state. Moreover, in the present case, the transferability of the potential parameters determined for the case of RDX crystal to all the nitramines considered in this study is assumed.

In the present treatment, the intermolecular interactions between the molecules of the crystal as the sum of pairwise Buckingham (6-exp) (repulsion and dispersion) and Coulombic (C) potentials is approximated:

$$V_{\alpha\beta}^{6-exp}(r) = A_{\alpha\beta}\exp(-B_{\alpha\beta}r) - C_{\alpha\beta}/r^6, \tag{1}$$

and

$$V_{\alpha\beta}^{C}(r) = \frac{q_\alpha q_\beta}{4\pi\varepsilon_0 r}, \tag{2}$$

where r is the interatomic distance between atoms α and β, q_α and q_β are the electrostatic charges on the atoms, and ε_0 is the dielectric permittivity constant of vacuum.

The parameters for the 6-exp potential in equation (1) are those previously determined for the case of the RDX crystal [1]. The same combination rules are used for the calculation of the heteroatom parameters from homoatom parameters, as previously reported [1].

The assignment of the electrostatic charges is made by using the set of atom-centered monopole charges for the isolated molecule that best reproduces the quantum mechanically derived electrostatic potential, which is calculated over grid points surrounding the van der Waals surface of the molecules. This method of fitting the electrostatic potential was proposed by Breneman and Wiberg [13] and is incorporated in the *Gaussian 94* package of programs [21] under the keyword CHELPG (electrostatic-potential-derived atomic charges). This method has the advantage of a higher density of points and a better selection procedure, which ensures a significant decrease in orientation effects compared to those observed with similar methods [12].

The CHELPG charges were found to be invariant to either the rotation of the molecular coordinates or internal bond rotations. These calculations have been done at both the HF [14] and second-order MP2 [15–18] levels to investigate the effect of electron correlation.

For the purpose of comparison and as an alternative to the computationally demanding MP2 method, density functional theory (DFT) has also been used in the Kohn-Sham formulation [22]. The DFT methods offer a less expensive but still accurate computational alternative to *ab initio* methods for including the electron correlation in post-HF treatments. In particular, the exchange functional, described by the fitted three-parameter hybrid of Becke [16] and the correlation functional of Lee, Yang, and Parr (B3LYP) [17] was employed. All the aformentioned theoretical calculations were done using a reasonable quality basis set (i.e., 6-31G** [split-valence plus d-type and p-type polarization functions]) [24].

It has been shown previously [25, 26] that the neglect of electron correlation in self-consistent wave functions overestimates the electrostatic interactions; however, this is mainly a scaling effect. Cox and Williams [25] have suggested that a scaling factor of 0.9 can be used to improve agreement between the calculated and experimental values of the dipole moments for a set of eight small molecules. The same factor has been justified in a study of the electrostatic interactions of a dipeptide [26], as well as in a more recent work related to the role of electrostatic interactions in determining the crystal structures of polar organic molecules [10]. Such an electrostatic model has been employed to further evaluate the effects of this scaling procedure. Specifically, four electrostatic models were tested for each of the 30 crystals. Two of them use electron correlation methods (namely MP2 and B3LYP); the third one uses unscaled HF charges, and the last HF charges scaled by 0.9 (denoted as 0.9HF).

3. Computational Approach

A general procedure for testing intermolecular potential energy functions for organic crystals is based on the use of molecular packing calculations [5, 6]. The basic idea is to minimize the

lattice energy with respect to the structural degrees of freedom of the crystal. For crystals with one molecule in the asymmetric unit occupying an arbitrary position, the maximum number of degrees of freedom is 12 and corresponds to the six unit cell constants (a, b, c, α, β, γ), the three rotations (θ_1, θ_2, θ_3) and the three translations (τ_1, τ_2, τ_3) of the rigid molecule. A reduced number of structural degrees of freedom might be involved, depending on the symmetry restrictions of different space groups. For crystals with more than one molecule in the asymmetric unit, additional degrees of freedom are introduced to describe the rotation and translation of the additional molecules.

Assuming that the crystal energy is known as a function of the structural lattice parameters, the equilibrium crystal configuration is determined by the conditions of zero force and torque, together with the requirement that there is a minimum. The search for such a minimum can be done using a combination of steepest-descent and Newton-Raphson procedures [27, 28].

In the present study, it is assumed that the crystals can be represented as an ensemble of rigid molecules. The minimization of the lattice energy with symmetry constraints has been performed using the molecular packing program PCK91 [29] by taking the experimentally observed geometries as starting configurations. This program employs an accelerated convergence method [1, 28] for accurate evaluation of the crystal Coulombic and dispersion lattice sums, with the first and second derivatives of the crystal energy evaluated analytically. In all calculations, a cutoff distance of 19 Å has been used with the parameters η that determines the relative contributions of the real- and reciprocal-space terms as defined in Sorescu et al. [1] having the values $\eta_1 = 0.1861$ Å^{-1} and $\eta_6 = 0.2304$ Å^{-1}. The space-group symmetry is maintained throughout the energy minimization. This reduces the number of independent variables in the minimization procedure, resulting in a significant decrease in the computational time compared to unconstrained energy minimization. For example, for the β-phase of HMX crystal with space group $P2_1/n$ (Z = 2), the crystallographic parameters that were varied in the minimization using the PCK91 program are the three dimensions of the unit cell and the angle β, while the angles α and γ were frozen at 90°. Since the molecule in the asymmetric unit occupies an inversion

center, only the three rotations of this molecule were allowed to vary, while the three translations were not modified to maintain the symmetry imposed by the inversion center. It has been previously shown [1, 2, 30] that, despite the symmetry restrictions imposed in the PCK91 program, the final lattice energies and crystallographic parameters are in good agreement with those obtained when symmetry constraints were removed (i.e., the predicted crystals maintained the observed space-group symmetry).

The quality of the predicted geometrical crystallographic parameters relative to the experimental values has been done using a structural shift factor of the form [28, 31]

$$F = (\Delta\theta/2)^2 + (10\Delta x)^2 + (100\Delta a/a)^2 + (100\Delta b/b)^2 + (100\Delta c/c)^2 + (\Delta\alpha)^2 + (\Delta\beta)^2 + (\Delta\gamma)^2, \quad (3)$$

where $\Delta\theta$ is the total root-mean-square (rms) rigid-body rotational displacement (in degrees) after minimization; Δx is the rms total rigid-body translational displacement (in angstroms); and a, b, c, and a, β, γ are, respectively, the lengths of the edges and the angles of the unit cell.

An important test of the validity of the model is the accuracy of the predicted lattice energies of the crystals. The lattice energies determine the relative stabilities of the different crystallographic phases. The calculated static lattice energy can be compared to the experimental sublimation enthalpy by the using the relationship [32] $-\Delta H_{subl} = E + K_0 + 2RT$, where E is the lattice energy and K_0 is the zero-point energy. Often, a rough estimation of the lattice energy is obtained by neglecting the K_0 term. Kitaigorodski [5] has pointed out that, considering the inaccuracy involved in the experimental determination of ΔH_{sub} and with the neglect of zero-point energy, discrepancies up to 3–4 kcal/mol between the calculated and the observed enthalpies of sublimation are expected [5]. In the case of RDX crystals, it was found, using this approximation, that the predicted lattice energy ($E = -130.09$ kJ/mol) is in very close agreement with the experimental sublimation enthalphy ($-\Delta H_{sub} = -130.1$ kJ/mol) [1].

4. Results and Discussions

The 30 nitramine molecules considered in this study are shown in Figure 1. They were chosen as representative examples of important acyclic and cyclic nitramines. Different types of mono- and polycyclic nitramines have been included, particularly crystals that are important energetic materials. The structures of most of these crystals have been obtained by x-ray diffraction techniques. Despite the generally poorer resolution of hydrogen atom positions obtained by these techniques, no additional adjustment of these positions has been done to give, for example, the standard bond lengths [33]. The crystal structures in Figure 1 are denoted first by the common names of the molecules. Where available, the crystal abbreviation from the original reference is also included with the corresponding crystal "refcode" used in the Cambridge Structural Database [34] and indicated by the term in the second set of parentheses. The structures used for HNIW [35] and β-HMX [36] crystals are not in the Cambridge database, so they do not have a refcode. In addition, different crystallographic phases of HMX and HNIW crystals have been studied; these are detailed in Table 1. The specific references for each of the 30 crystals in Table 1 are provided in brackets in the "Crystal" column and found in the reference section [35–57].

The results of MP calculations using the PCK91 program are presented in Table 1. The predicted structural lattice parameters for the great majority of these crystals deviate by less than 2% from the experimental structures. Also, for the majority of the crystals, there are small rotations and practically no translations for the molecules in the asymmetric unit cell. The accuracy of the predictions can be seen in Figure 2, where the overall structural drift factors described in equation (3) are given. Only 10% of the total number of crystals considered here have a structural shift factor larger than 2.0, and practically half of the crystals have shift factors that are less than 1.0.

It is important to point out that, ideally, the predicted lattice structural parameters should be compared with the values determined at zero temperature. However, this is not possible due to

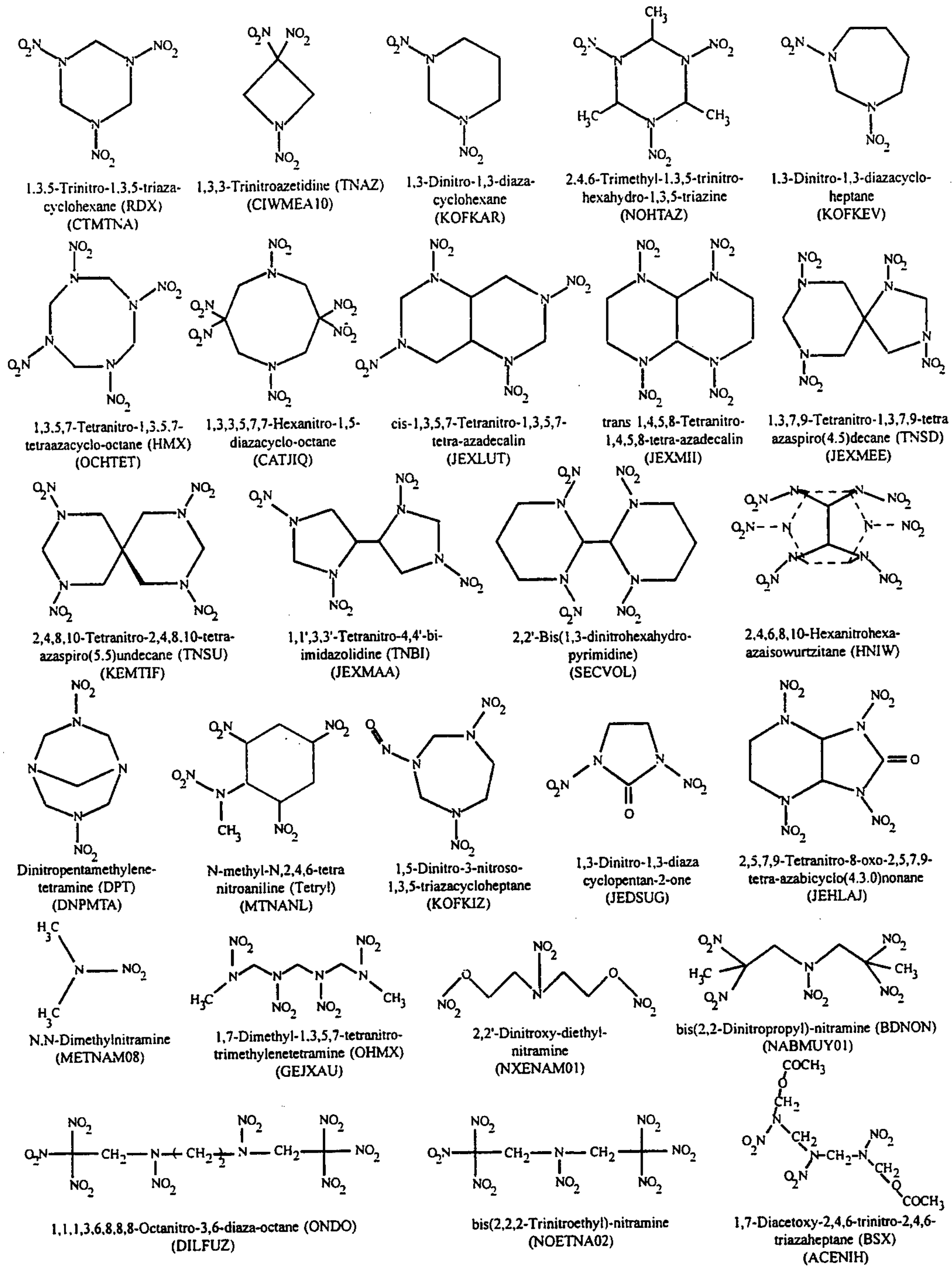


Figure 1. Illustration of Molecules Whose Crystal Structures Were Studied. The Common Abbreviation of the Crystal Name Is Given in the First Set of Parentheses, and the Refcode Entry of the Cambridge Structural Database [34] Is Given in the Second Set of Parentheses.

Table 1. Comparison of the Crystallographic Parameters as Determined in Molecular Packing Calculations to the Corresponding Experimental Values for Different Molecular Structures

Data Set	Crystal	Symm.	Z	a (Å)	b (Å)	c (Å)	(°)[a]	(°)	x(Å)[b]	F[c]
1	CTMTNA [37]	Pbca	8	13.1820	11.5740	10.7090	90.0			
	I			13.2862 (0.8)	11.6511 (0.7)	10.6081 (−0.9)	90.0	1.240	0.126	0.886
	II			13.2691 (0.7)	11.6341 (0.5)	10.6128 (−0.9)	90.0	1.470	0.129	0.863
	III			13.2600 (0.6)	11.6260 (0.4)	10.6103 (−0.9)	90.0	1.365	0.127	0.835
	IV			13.2236 (0.3)	11.5853 (0.1)	10.5948 (−1.1)	90.0	1.199	0.121	0.783
2	CIWMEA10 [38]	Pbca	8	5.7330	11.1270	21.4960	90.0			
	I			5.7691 (0.6)	11.0676 (−0.5)	21.2537 (−1.1)		0.927	0.073	0.735
	II			5.7550 (0.4)	11.0602 (−0.6)	21.2597 (−1.1)	0.886	0.063	0.679	
	III			5.7366 (0.1)	11.0711 (−0.5)	21.2697 (−1.1)	1.067	0.055	0.624	
	IV			5.7007 (−0.6)	11.0707 (−0.5)	21.3017 (−0.9)		1.386	0.025	0.622
3	KOFKAR [39]	P21/c	4	6.630	21.390	6.060	120.0			
	I			6.5556 (−1.1)	20.3153 (−5.0)	5.9076 (−2.5)	115.60 (−3.7)	0.772	0.684	4.063
	II			6.5499 (−1.2)	20.3381 (−4.9)	5.8968 (−2.7)	115.61 (−3.7)	0.775	0.669	4.021
	III			6.5468 (−1.3)	20.3382 (−4.9)	5.8978 (−2.7)	115.60 (−3.7)	0.773	0.669	4.023
	IV			6.5221 (−1.6)	20.4265 (−4.5)	5.8775 (−3.0)	115.95 (−3.4)	0.519	0.615	3.792
4	NOHTAZ [40]	$P2_12_12_1$	4	7.31	10.732	14.155	90.0			
	I			7.2433 (−0.9)	10.8359 (1.0)	13.8592 (−2.1)		1.026	0.133	1.279
	II			7.2360 (−1.0)	10.8401 (1.0)	13.8364 (−2.3)		1.039	0.143	1.372
	III			7.2340 (−1.0)	18.8413 (1.0)	13.8330 (−2.3)		0.963	0.144	1.386
	IV			7.2171 (−1.3)	10.8402 (1.0)	13.7809 (−2.6)		0.874	0.150	1.553
5	KOFKEV [39]	P21/n	4	8.7380	11.200	8.3830	90.1			
	I			8.6594 (−0.9)	11.0612 (−1.2)	8.3520 (−0.4)	90.5 (0.4)	0.755	0.123	0.846

Note: The first line of every data set represents the corresponding experimental value. The Roman symbols I, II, III, and IV denote the results obtained for electrostatic charges calculated at MP2/6-31G**, B3LYP/6-31G**, HF/6-31G**, and scaled by 0.9, and respectively at HF/6-31G** and unscaled. The values in parentheses represent the procentual difference relative to experimental values.

[a] For monoclinic systems, only angles are given. For triclinic systems, the cell angles and the cell angle errors are given in the order. For orthorhombic crystal systems, a value of 90.0 is indicated only for the experimental structure.

[b] x = the net rotation of the molecule and the net translation of the center of mass of the molecule.

[c] F = structural shift factor; defined in equation (3).

Table 1. Comparison of the Crystallographic Parameters as Determined in Molecular Packing Calculations to the Corresponding Experimental Values for Different Molecular Structures (continued)

Data Set	Crystal	Symm.	Z	a (Å)	b (Å)	c (Å)	(°)[a]	(°)	x(Å)[b]	F[c]
	II			8.6657 (−0.8)	11.0522 (−1.3)	8.3447 (−0.5)	90.48 (0.4)	0.885	0.122	0.862
	III			8.6623 (−0.9)	11.0531 (−1.3)	8.3464 (−0.4)	90.47 (0.4)	0.799	0.122	0.861
	IV			8.6480 (−1.0)	11.0359 (−1.5)	8.3312 (−0.6)	90.32 (0.2)	0.696	0.120	0.936
6	-HMX [36]	P21/n	2	6.5347	11.0296	7.3549	102.689			
	I			6.4756 (−0.9)	10.8316 (−1.8)	7.3733 (0.2)	99.91 (−2.7)	1.662	0.000	1.583
	II			6.4649 (−1.1)	10.8171 (−1.9)	7.3836 (0.4)	100.05 (−2.6)	1.769	0.000	1.595
	III			6.4679 (−1.0)	10.8129 (−2.0)	7.3797 (0.3)	100.13 (−2.5)	1.696	0.000	1.567
	IV			6.4563 (−1.2)	10.7626 (−2.4)	7.3965 (0.6)	100.63 (−2.0)	1.957	0.000	1.602
7	OCHTET [41] (HMX, -form)	Fdd2	8	15.1400	23.8900	5.9130	90.0			
	I			14.9760 (−1.1)	23.6617 (−1.0)	6.0191 (1.8)		2.502	0.019	1.314
	II			14.9775 (−1.1)	23.6502 (−1.0)	6.0115 (1.7)		2.321	0.018	1.256
	III			14.9668 (−1.1)	23.6496 (−1.0)	6.0065 (1.6)		2.268	0.017	1.239
	IV			14.9452 (−1.3)	23.6373 (−1.1)	5.9819 (1.2)		1.840	0.012	1.117
8	OCHTET03 [42] (HMX, -form)	P61	6	7.7110	7.7110	32.5530	120.0[d]			
	I			7.6681 (−0.6)	7.6681 (−0.6)	33.5947 (3.2)		2.404	0.111	1.645
	II			7.6647 (−0.6)	7.6647 (−0.6)	33.5503 (3.1)		2.394	0.110	1.597
	III			7.6688 (−0.5)	7.6688 (−0.5)	33.4853 (2.9)		2.266	0.095	1.482
	IV			7.6666 (−0.6)	7.6666 (−0.6)	33.2954 (2.3)		2.023	0.084	1.233
9	CATJIQ [43]	Pbca	4	11.289	10.205	11.880	90.0			
	I			11.5194 (2.0)	9.8602 (−3.4)	11.7061 (−1.5)		7.117	0.087	2.496

Note: The first line of every data set represents the corresponding experimental value. The Roman symbols I, II, III, and IV denote the results obtained for electrostatic charges calculated at MP2/6-31G**, B3LYP/6-31G**, HF/6-31G**, and scaled by 0.9, and respectively at HF/6-31G** and unscaled. The values in parentheses represent the procentual difference relative to experimental values.

[a] For monoclinic systems, only angles are given. For triclinic systems, the cell angles and the cell angle errors are given in the order. For orthorhombic crystal systems, a value of 90.0 is indicated only for the experimental structure.

[b] x = the net rotation of the molecule and the net translation of the center of mass of the molecule.

[c] F = structural shift factor; defined in equation (3).

[d] For P31 and P61, the angle = 120 is indicated.

Table 1. Comparison of the Crystallographic Parameters as Determined in Molecular Packing Calculations to the Corresponding Experimental Values for Different Molecular Structures (continued)

Data Set	Crystal	Symm.	Z	a (Å)	b (Å)	c (Å)	(°)[a]	(°)	x(Å)[b]	F[c]
	II			11.5106 (2.0)	9.8526 (−3.5)	11.6979 (−1.5)		6.992	0.091	2.497
	III			11.5114 (2.0)	9.8190 (−3.8)	11.6898 (−1.6)		6.743	0.095	2.570
	IV			11.4907 (1.8)	9.7801 (−4.2)	11.6735 (−1.7)		6.530	0.103	2.656
10	JEXLUT [44]	P21	2	7.471	10.7770	7.6420	103.34			
	I			7.3400 (−1.8)	10.6501 (−1.2)	7.6707 (0.4)	105.02 (1.1)	1.490	0.141	1.193
	II			7.3298 (−1.9)	10.6430 (−1.2)	7.6675 (0.3)	104.97 (1.1)	1.536	0.147	1.241
	III			7.3260 (−1.9)	10.6426 (−1.2)	7.6650 (0.3)	104.92 (1.0)	1.531	0.149	1.250
	IV			7.3114 (−2.1)	10.6174 (−1.5)	7.6604 (0.2)	104.81 (0.9)	1.560	0.162	1.354
11	JEXMII [44]	P1	1	6.4610	6.8450	7.5420	74.01 75.00 68.53			
	I			6.3721 (−1.4)	6.9609 (1.7)	7.3407 (−2.7)	73.94 (−0.1) 72.63 (−3.2) 68.91 (0.6)	2.146	0.194	1.796
	II			6.3803 (−1.2)	6.9531 (1.6)	7.3284 (−2.8)	74.04 (0.0) 72.44 (−3.4) 69.42 (1.3)	1.867	0.215	1.888
	III			6.3517 (−1.7)	6.9355 (1.3)	7.3263 (−2.9)	74.17 (0.2) 73.00 (−2.7) 69.16 (0.9)	2.036	0.183	1.756
	IV			6.3330 (−2.0)	6.9279 (1.2)	7.3052 (−3.1)	74.47 (0.6) 73.14 (−2.5)	2.082	0.195	1.901

Note: The first line of every data set represents the corresponding experimental value. The Roman symbols I, II, III, and IV denote the results obtained for electrostatic charges calculated at MP2/6-31G**, B3LYP/6-31G**, HF/6-31G**, and scaled by 0.9, and respectively at HF/6-31G** and unscaled. The values in parentheses represent the procentual difference relative to experimental values.

[a]For monoclinic systems, only angles are given. For triclinic systems, the cell angles and the cell angle errors are given in the order. For orthorhombic crystal systems, a value of 90.0 is indicated only for the experimental structure.

[b]x = the net rotation of the molecule and the net translation of the center of mass of the molecule.

[c]F = structural shift factor; defined in equation (3).

Table 1. Comparison of the Crystallographic Parameters as Determined in Molecular Packing Calculations to the Corresponding Experimental Values for Different Molecular Structures (continued)

Data Set	Crystal	Symm.	Z	a (Å)	b (Å)	c (Å)	(°)[a]	(°)	x(Å)[b]	F[c]
							69.74 (1.8)			
12	JEXMEE [44]	$P2_12_12_1$	4	7.8630	10.9890	14.4700	90.0			
	I			7.7809 (−1.0)	10.9187 (−0.6)	14.5671 (0.7)		1.327	0.094	0.810
	II			7.7697 (−.12)	10.9007 (−0.8)	14.5770 (0.7)		1.314	0.096	0.889
	III			7.7660 (−1.2)	10.8989 (−0.8)	14.5772 (0.7)		1.265	0.096	0.902
	IV			7.7463 (−1.5)	10.8664 (−1.1)	14.5575 (0.60)		1.384	0.094	1.017
13	KEMTIF [45]	C2/c	8	12.8310	10.7260	19.6440	108.13			
	I			12.8427 (0.1)	10.6040 (−1.1)	19.5672 (−0.4)	108.65 (0.5)	0.454	0.155	0.833
	II			12.8249 (0.0)	10.5976 (−1.2)	19.5465 (−0.5)	108.58 (0.4)	0.480	0.151	0.839
	III			12.8210 (−0.1)	10.5913 (−1.3)	19.5453 (−0.5)	108.56 (0.4)	0.478	0.152	0.885
	IV			12.7957 (−0.3)	10.5541 (−1.6)	19.5084 (−0.7)	108.39 (0.2)	0.527	0.149	0.957
14	JEXMAA [44]	$P2_12_12_1$	4	6.5480	9.89860	19.2990	90.0			
	I			6.5140 (-0.5)	9.8934 (0.0)	19.1302 (−0.9)		1.528	0.135	0.831
	II			6.5046 (−0.7)	9.8787 (−0.2)	19.1315 (−0.9)		1.593	0.139	0.869
	III			6.5066 (−0.6)	9.8729 (−0.2)	19.1448 (−0.8)		1.574	0.131	0.828
	IV			6.4863 (−0.9)	9.8471 (−0.5)	19.1517 (−0.8)		1.561	0.138	0.918
15	SECVOL [43]	P1	1	6.6020	7.3410	8.2310	89.54 74.56 66.15			
	I			6.4829 (−1.8)	7.2459 (−1.3)	8.1550 (−0.9)	89.18 (−0.4) 74.38 (−0.2) 66.76 (0.9)	0.648	0.102	1.032

Note: The first line of every data set represents the corresponding experimental value. The Roman symbols I, II, III, and IV denote the results obtained for electrostatic charges calculated at MP2/6-31G**, B3LYP/6-31G**, HF/6-31G**, and scaled by 0.9, and respectively at HF/6-31G** and unscaled. The values in parentheses represent the procentual difference relative to experimental values.

[a]For monoclinic systems, only angles are given. For triclinic systems, the cell angles and the cell angle errors are given in the order. For orthorhombic crystal systems, a value of 90.0 is indicated only for the experimental structure.

[b]x = the net rotation of the molecule and the net translation of the center of mass of the molecule.

[c]F = structural shift factor; defined in equation (3).

Table 1. Comparison of the Crystallographic Parameters as Determined in Molecular Packing Calculations to the Corresponding Experimental Values for Different Molecular Structures (continued)

Data Set	Crystal	Symm.	Z	a (Å)	b (Å)	c (Å)	(°)[a]	(°)	x(Å)[b]	F[c]
	II			6.4802 (−1.8)	7.2362 (−1.4)	8.1431 (−1.1)	89.10 (−0.5) 74.47 (−0.1) 66.79 (1.0)	0.756	0.110	1.106
	III			6.4663 (−2.1)	7.2347 (−1.4)	8.1559 (−0.9)	89.14 (−0.4) 74.40 (−0.2) 66.86 (1.1)	0.891	0.115	1.156
	IV			6.4332 (−2.6)	7.2131 (−1.7)	8.1506 (−1.0)	89.16 (−0.4) 74.55 (0.0) 67.03 (1.3)	1.291	0.149	1.419
16	-HNIW [35]	$P2_1/n$	4	8.8278	12.5166	13.3499	106.752			
	I			8.8578 (0.3)	12.4881 (−0.2)	13.4631 (0.8)	105.13 (−1.5)	1.932	0.140	1.033
	II			8.8466 (0.2)	12.4792 (−0.3)	13.4489 (0.7)	106.75 (−1.5)	1.964	0.137	1.009
	III			8.8334 (0.1)	12.4924 (−0.2)	13.4371 (0.7)	105.15 (−1.5)	1.876	0.138	0.986
	IV			8.8063 (−0.2)	12.4972 (−0.2)	13.3963 (0.3)	105.21 (−1.4)	1.780	0.141	0.945
17	-HNIW [35]	$Pb2_1a$	4	9.6764	13.0063	11.6493	90.0			
	I			9.5342 (−1.5)	12.9254 (−0.6)	11.7522 (0.9)		0.690	0.113	0.972
	II			9.5285 (−1.5)	12.9137 (−0.7)	11.7469 (0.8)		0.659	0.117	1.002
	III			9.5257 (−1.6)	12.9025 (−0.8)	11.7382 (0.8)		0.626	0.120	1.017
	IV			9.5171 (−1.6)	12.8807 (−1.0)	11.7154 (0.6)		0.419	0.126	1.059
18	-HNIW [35]	$P2_1/n$	4	13.2310	8.1700	14.8760	109.17			
	I			13.5148 (2.1)	7.9099 (−3.2)	14.9339 (0.4)	109.12 (0.0)	6.904	0.230	2.319
	II			13.4987 (2.0)	7.9090 (−3.2)	14.9148 (0.3)	109.10 (−0.1)	6.714	0.232	2.274

Note: The first line of every data set represents the corresponding experimental value. The Roman symbols I, II, III, and IV denote the results obtained for electrostatic charges calculated at MP2/6-31G**, B3LYP/6-31G**, HF/6-31G**, and scaled by 0.9, and respectively at HF/6-31G** and unscaled. The values in parentheses represent the procentual difference relative to experimental values.

[a] For monoclinic systems, only angles are given. For triclinic systems, the cell angles and the cell angle errors are given in the order. For orthorhombic crystal systems, a value of 90.0 is indicated only for the experimental structure.

[b] x = the net rotation of the molecule and the net translation of the center of mass of the molecule.

[c] F = structural shift factor; defined in equation (3).

Table 1. Comparison of the Crystallographic Parameters as Determined in Molecular Packing Calculations to the Corresponding Experimental Values for Different Molecular Structures (continued)

Data Set	Crystal	Symm.	Z	a (Å)	b (Å)	c (Å)	(°)[a]	(°)	x(Å)[b]	F[c]
	III			13.4836 (1.9)	7.9094 (−3.2)	14.8961 (0.1)	109.08 (−0.1)	6.591	0.233	2.241
	IV			13.4486 (1.6)	7.9096 (−3.2)	14.8584 (−0.1)	109.01 (−0.1)	6.225	0.241	2.175
19	DNPMTA [47]	$P2_1/c$	4	9.345	8.284	11.566	105.6			
	I			9.2282 (−1.3)	8.2258 (−0.7)	11.4319 (−1.2)	105.37 (−0.2)	1.204	0.030	0.807
	II			9.2415 (−1.1)	8.2346 (−0.6)	11.3959 (−1.5)	105.34 (−0.2)	1.222	0.036	0.848
	III			9.2377 (−1.1)	8.2298 (−0.7)	11.4089 (−1.4)	105.40 (−0.2)	1.221	0.034	0.828
	IV			9.2202 (−1.3)	8.2020 (−1.0)	11.4041 (−1.4)	105.57 (0.0)	1.372	0.038	0.943
20	MTNANL [48]	P21/c	4	14.1290	7.3740	10.6140	95.07			
	I			13.7905 (−2.4)	7.3776 (0.0)	10.6515 (0.4)	94.35 (−0.8)	0.302	0.166	1.236
	II			13.7998 (−2.3)	7.3607 (−0.2)	10.6446 (0.3)	94.33 (−0.8)	0.259	0.165	1.212
	III			13.7958 (−2.4)	7.3532 (−0.3)	10.6319 (0.2)	94.36 (−0.7)	0.323	0.163	1.216
	IV			13.8256 (−2.1)	7.3265 (−0.6)	10.5854 (−0.3)	94.42 (−0.7)	0.388	0.159	1.160
21	KOFKIZ [39]	Pc	4	11.300	6.340	12.230	102.40			
	I			11.5003 (1.8)	6.2393 (−1.6)	12.3482 (1.0)	102.58 (0.2)	4.443	0.180	1.508
								0.420	0.104	
	II			11.4945 (1.7)	6.2486 (−1.4)	12.3206 (0.7)	102.71 (0.3)	4.372	0.147	1.406
								0.603	0.106	
	III			11.5197 (1.9)	6.2452 (−1.5)	12.3198 (0.7)	102.90 (0.5)	4.453	0.140	1.482
								0.583	0.125	
	IV			11.4859 (1.6)	6.2486 (−1.4)	12.2657 (0.3)	103.04 (0.6)	4.406	0.096	1.346
								0.817	0.121	
22	JEDSUG [49]	$P2_12_12_1$	4	5.9120	7.9280	13.9510	90.0			

Note: The first line of every data set represents the corresponding experimental value. The Roman symbols I, II, III, and IV denote the results obtained for electrostatic charges calculated at MP2/6-31G**, B3LYP/6-31G**, HF/6-31G**, and scaled by 0.9, and respectively at HF/6-31G** and unscaled. The values in parentheses represent the procentual difference relative to experimental values.

[a] For monoclinic systems, only angles are given. For triclinic systems, the cell angles and the cell angle errors are given in the order. For orthorhombic crystal systems, a value of 90.0 is indicated only for the experimental structure.

[b] x = the net rotation of the molecule and the net translation of the center of mass of the molecule.

[c] F = structural shift factor; defined in equation (3).

Table 1. Comparison of the Crystallographic Parameters as Determined in Molecular Packing Calculations to the Corresponding Experimental Values for Different Molecular Structures (continued)

Data Set	Crystal	Symm.	Z	a (Å)	b (Å)	c (Å)	(°)[a]	(°)	x(Å)[b]	F[c]
	I			5.9731 (1.0)	7.8660 (−0.8)	13.7991 (−1.1)		2.614	0.096	1.049
	II			5.9646 (0.9)	7.8495 (−1.0)	13.8041 (−1.1)		2.469	0.093	1.027
	III			5.9576 (0.8)	7.8449 (−1.0)	13.7986 (−1.1)		2.399	0.097	1.026
	IV			5.9220 (0.2)	7.8140 (−1.4)	13.8098 (−1.0)		2.029	0.089	0.994
23	JEHLAJ [50]	P31	3	10.9230	10.9230	7.8880	120.0[d]			
	I			10.8959 (−0.2)	10.8959 (−0.2)	7.9315 (0.6)		1.463	0.037	0.369
	II			10.8808 (−0.3)	10.8808 (−0.4)	7.9234 (0.4)		1.436	0.027	0.467
	III			10.8737 (−0.5)	10.8735 (−0.5)	7.9132 (0.3)		1.367	0.021	0.451
	IV			10.8417 (−0.7)	10.8417 (−0.7)	7.8970 (0.1)		1.208	0.009	0.547
24	METNAM08 [51]	P21/m	2	6.540	6.195	6.060	123.65			
	I			6.6364 (1.5)	6.2481 (0.9)	6.2207 (2.7)	124.08 (0.3)	0.212	0.084	1.472
	II			6.6380 (1.5)	6.2391 (0.7)	6.2211 (2.7)	124.09 (0.4)	0.255	0.083	1.465
	III			6.6345 (1.4)	6.2424 (0.8)	6.2273 (2.8)	124.07 (0.3)	0.186	0.089	1.502
	IV			6.6179 (1.2)	6.2179 (0.4)	6.2092 (2.5)	123.94 (0.2)	0.105	0.082	1.294
25	GEJXAU [52]	P21/c	4	20.9520	9.4770	6.5710	96.29			
	I			20.8355 (−0.6)	9.3867 (−1.0)	6.4843 (−1.3)	96.80 (0.5)	1.706	0.098	0.905
	II			20.8601 (−0.4)	9.3693 (−1.1)	6.4801 (−1.4)	96.64 (0.4)	1.734	0.102	0.941
	III			20.8566 (−0.5)	9.3744 (−1.1)	6.4740 (−1.5)	96.73 (0.5)	1.637	0.099	0.914
	IV			20.8399 (−0.5)	9.3484 (−1.4)	6.4494 (−1.4)	96.89 (0.6)	1.274	0.097	1.100
26	NXENAM01 [53]	P21/c	4	9.060	9.150	12.330	109.940			
	I			9.0568 (0.0)	9.0915 (−0.6)	12.3615 (0.3)	110.50 (0.5)	1.705	0.027	0.515
	II			9.0452 (−0.2)	9.0928 (−0.6)	12.3436 (0.1)	110.40 (0.4)	1.678	0.031	0.491

Note: The first line of every data set represents the corresponding experimental value. The Roman symbols I, II, III, and IV denote the results obtained for electrostatic charges calculated at MP2/6-31G**, B3LYP/6-31G**, HF/6-31G**, and scaled by 0.9, and respectively at HF/6-31G** and unscaled. The values in parentheses represent the procentual difference relative to experimental values.

[a]For monoclinic systems, only angles are given. For triclinic systems, the cell angles and the cell angle errors are given in the order. For orthorhombic crystal systems, a value of 90.0 is indicated only for the experimental structure.

[b]x = the net rotation of the molecule and the net translation of the center of mass of the molecule.

[c]F = structural shift factor; defined in equation (3).

[d]For P31 and P61, the angle = 120 is indicated.

Table 1. Comparison of the Crystallographic Parameters as Determined in Molecular Packing Calculations to the Corresponding Experimental Values for Different Molecular Structures (continued)

Data Set	Crystal	Symm.	Z	a (Å)	b (Å)	c (Å)	(°)[a]	(°)	x (Å)[b]	F[c]
	III			9.0467 (−0.1)	9.0813 (−0.8)	12.3390 (0.1)	110.42 (0.4)	1.589	0.032	0.509
	IV			9.0444 (0.2)	9.0477 (−1.1)	12.3149 (−0.1)	110.40 (0.4)	1.465	0.039	0.605
27	NABMUY01 [54]	C2	2	10.7260	5.9920	10.4000	110.01			
	I			10.5180 (−1.9)	5.9524 (−0.7)	10.3705 (−0.3)	109.77 (−0.2)	0.333	0.011	0.935
	II			10.5058 (−2.10)	5.9488 (−0.7)	10.3650 (−0.3)	109.72 (−0.3)	0.228	0.012	0.996
	III			10.4796 (−2.3)	5.9423 (−0.8)	10.3658 (−0.3)	109.63 (0.3)	0.000	0.014	1.117
	IV			10.4440 (−2.6)	5.9223 (−1.2)	10.3586 (−0.4)	109.50 (−0.5)	0.307	0.019	1.322
28	DILFUZ [55]	P21/n	2	5.9716	12.0170	11.8407	97.114			
	I			5.9169 (−0.9)	12.0507 (0.3)	11.4238 (−3.5)	95.98 (−1.2)	0.786	0.017	1.720
	II			5.9120 (−1.0)	12.0456 (0.2)	11.4207 (−3.5)	95.97 (−1.2)	0.741	0.014	1.737
	III			5.9094 (−1.0)	12.0530 (0.3)	11.3882 (−3.8)	95.78 (−1.4)	0.829	0.018	1.883
	IV			5.8901 (−1.4)	12.0476 (0.3)	11.3627 (−4.0)	95.65 (−1.5)	0.754	0.015	2.027
29	NOETNA02 [56]	P21/n	4	11.8200	6.1620	18.2290	96.10			
	I			11.7226 (−0.8)	6.0508 (−1.8)	17.7506 (−2.6)	95.49 (−0.6)	1.258	0.17	1.570
	II			11.7311 (−0.8)	6.0453 (−1.9)	17.7284 (−2.7)	95.42 (−0.7)	1.308	0.187	1.638
	III			11.7152 (−0.9)	6.0407 (−2.0)	17.7191 (−2.8)	95.36 (−0.8)	1.254	0.197	1.697
	IV			11.6977 (−1.0)	6.0219 (−2.3)	17.7022 (−2.9)	95.30 (−0.8)	1.291	0.219	1.846
30	ACENIH [57]	C2/c	4	26.9350	9.1740	6.1220	101.90			
	I			26.7831 (−0.6)	9.2170 (0.5)	5.9955 (−2.1)	101.78 (0.4)	0.204	0.036	0.925
	II			26.7718 (−0.6)	9.2189 (0.5)	5.9895 (−2.2)	101.77 (0.4)	0.221	0.083	0.968
	III			26.7416 (−0.7)	9.2046 (0.3)	5.9938 (−2.1)	191.67 (0.3)	0.103	0.037	0.936
	IV			26.6814 (−0.9)	9.1524 (−0.2)	5.9979 (−2.0)	101.44 (0.1)	0.133	0.043	0.935

Note: The first line of every data set represents the corresponding experimental value. The Roman symbols I, II, III, and IV denote the results obtained for electrostatic charges calculated at MP2/6-31G**, B3LYP/6-31G**, HF/6-31G**, and scaled by 0.9, and respectively at HF/6-31G** and unscaled. The values in parentheses represent the procentual difference relative to experimental values.

[a]For monoclinic systems, only angles are given. For triclinic systems, the cell angles and the cell angle errors are given in the order. For orthorhombic crystal systems, a value of 90.0 is indicated only for the experimental structure.

[b]x = the net rotation of the molecule and the net translation of the center of mass of the molecule.

[c]F = structural shift factor; defined in equation (3).

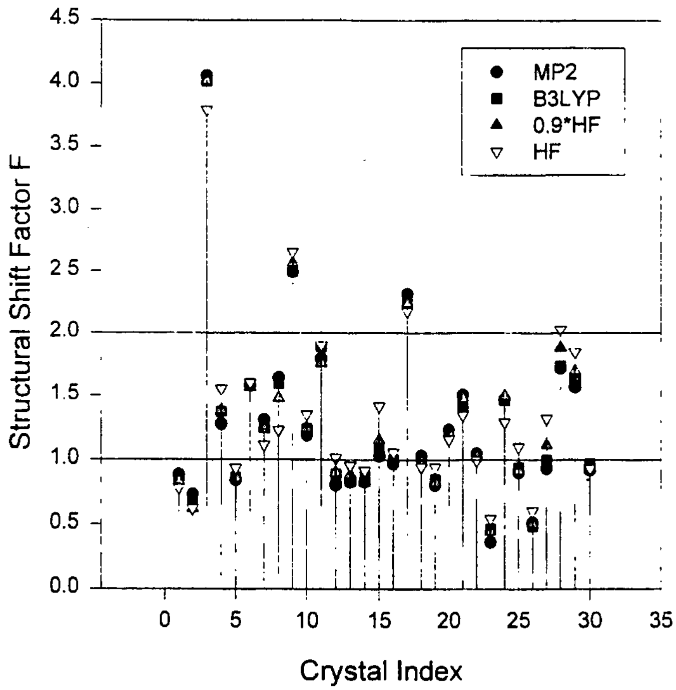


Figure 2. The Calculated Structural Shift Factor F (Equation [3]) for the Crystal Structures. The Crystal Index Corresponds to the Number of the Crystal in Table 1. The Horizontal Lines at 1 and 2 Are Marked for a Clearer View of the Distribution of Points.

lack of data at low temperatures. Consequently, the aforementioned comparison considers the deviations of the predicted geometrical parameters from the experimental values obtained at room temperature. It can be observed from the data given in Table 1 that the predicted lattice dimensions either underestimate or overestimate the experimental values. Consequently, there is not a general trend of the relationship between the predicted and the experimental geometric lattice periods, despite the small deviations between the two sets of values.

The influence of the level of *ab initio* calculations on the final crystallographic paramenters is also illustrated by the results in Table 1. The difference in the predicted geometrical parameters is less than 1.0% when correlated and uncorrelated *ab initio* methods are used. In addition, there is not a clear trend of the degree of accuracy with the *ab initio* level of calculations. In 19 of the systems, the accuracy increases when the HF charges are replaced with those obtained at the

B3LYP and MP2 levels, but, in the other 11 cases, the accuracy decreases. The maximum difference of the structural shift factors with the different levels of calculation is less than 0.27%.

It can also be seen from the results in Table 1 that, when the electrostatic charges calculated at HF level are scaled by the 0.9 factor, the corresponding predicted geometrical parameters are very close to those obtained at MP2 level. Moreover, the corresponding structural shift factors have values intermediate between the MP2 and HF values.

The lattice energies predicted by different models are given in Table 2. As can be seen by comparing the results for MP2, B3LYP, and HF methods, the use of the correlated methods result in a decrease in the absolute lattice energy. This effect can be understood as a consequence of the decrease in the absolute value of the electrostatic energy, which is attractive. The variations in the absolutes values of the HF lattice energies are between 8.5 and 17.5%, relative to the MP2 energies, with the average deviation 12.8% (see Figure 3). The use of the 0.9 scaling factor reduces these deviations to the range 0–7.8%, with the average deviation 4.1%. Finally, the B3LYP lattice energies are, as expected, much closer to the MP2 energies, with the range of variations 1.5–3.9% and average deviation 2.6%. These results indicate that the lattice energies differ significantly for sets of electrostatic charges calculated with *ab initio* methods that do not include electron correlation. These differences can be decreased by a factor of ~3 by scaling the HF charges. Another important result is that DFT can provide charges that give an accuracy (within 2.6%) for the lattice energy that is comparable to those determined at the MP2 level. These results are important since the computational times for B3LYP calculations are significantly lower than those for MP2.

The calculated lattice energies can also be compared to experimental sublimation enthalpies in Table 2. For RDX (CTMTNA), HMX (β-HMX, OCHTET03) and dimethylnitramine (METNAM08) crystals the agreement of the MP2 energies to the experimental values is very good, while for tetryl (NTNANL) the difference of 15.7 kJ/mol is within the range 12–17 kJ/mol considered acceptable by Kitaigorodsky [5]. Despite the limited number of experimental values

Table 2. Comparison of the Experimental and Calculated Lattice Energies for Different Sets of Electrostatic Charges

No.	Crystal	ΔH_{sub} (kJ/mol)	Lattice Energies (kJ/mol)			
			MP2/6-31G**	B3LYP/6-31G**	0.9 HF/6-31G**	HF/6-31G**
1	CTMTNA	130.1 [58]	-130.09	-133.68	-136.05	-148.18
2	CIWMEA10		-113.01	-116.40	-118.81	-129.07
3	KOFKAR		-116.55	-119.40	-119.61	-129.26
4	NOHTAZ		-141.45	-145.35	-145.99	-157.25
5	KOFKEV		-120.00	-122.66	-122.20	-131.95
6	β-HMX	175.2 [58]	-180.23	-185.02	-187.01	-204.45
7	OCHTET		-179.15	-184.66	-188.74	-208.75
8	OCHTET03	161.9 [59]	-168.24	-173.44	-178.11	-197.67
9	CATJIQ		-182.50	-187.59	-196.88	-213.26
10	JEXLUT		-178.54	-184.32	-186.70	-200.43
11	JEXMII		-169.22	-172.11	-177.36	-190.98
12	JEXMEE		-172.98	-178.48	-179.86	-196.13
13	KEMTIF		-184.42	-190.46	-192.56	-208.80
14	JEXMAA		-176.33	-182.29	181.97	-196.64
15	SECVOL		-187.66	-192.30	-193.63	-209.42
16	HNIW (ε-phase)		-186.77	-192.82	-196.52	-210.88
17	HNIW (β-phase)		-181.29	-186.28	-190.54	-201.81
18	HNIW (γ-phase)		-175.31	-180.90	-186.15	-198.61
19	DNPMTA		-140.60	-142.78	-142.60	-154.30
20	MTNANL	133.8 ± 1.6 [60]	-149.53	-153.81	-158.30	-170.57
21	KOFKIZ		-262.18	-267.98	-265.78	-288.98
22	JEDSUG		-124.22	-128.89	-131.24	-145.14
23	JEHLAJ		-180.70	-187.76	-192.29	-209.63
24	METNAM08	69.87 [61]	-70.26	-71.20	-70.21	-76.25
25	GEJXAU		-171.87	-174.31	-175.69	-191.41
26	NXENAM01		-131.84	-134.80	-137.57	-148.40
27	NABMUY01		-169.28	-173.70	-180.86	-196.26
28	DILFUZ		-216.09	-220.50	-209.57	-241.50
29	NOETNA02		-166.55	-163.68	-172.29	-181.04
30	ACENIH		-186.20	-188.32	-191.61	-205.65

available for comparisons, it can be seen that a significant improvement in the accuracy of the predicted lattice energies can be obtained by using the electrostatic charges determined by electron correlated methods. The scaling of the HF charges also leads to improvements of the predicted energies, but the differences from the experimental values are larger than those obtained when the charges are calculated with electron correlation methods.

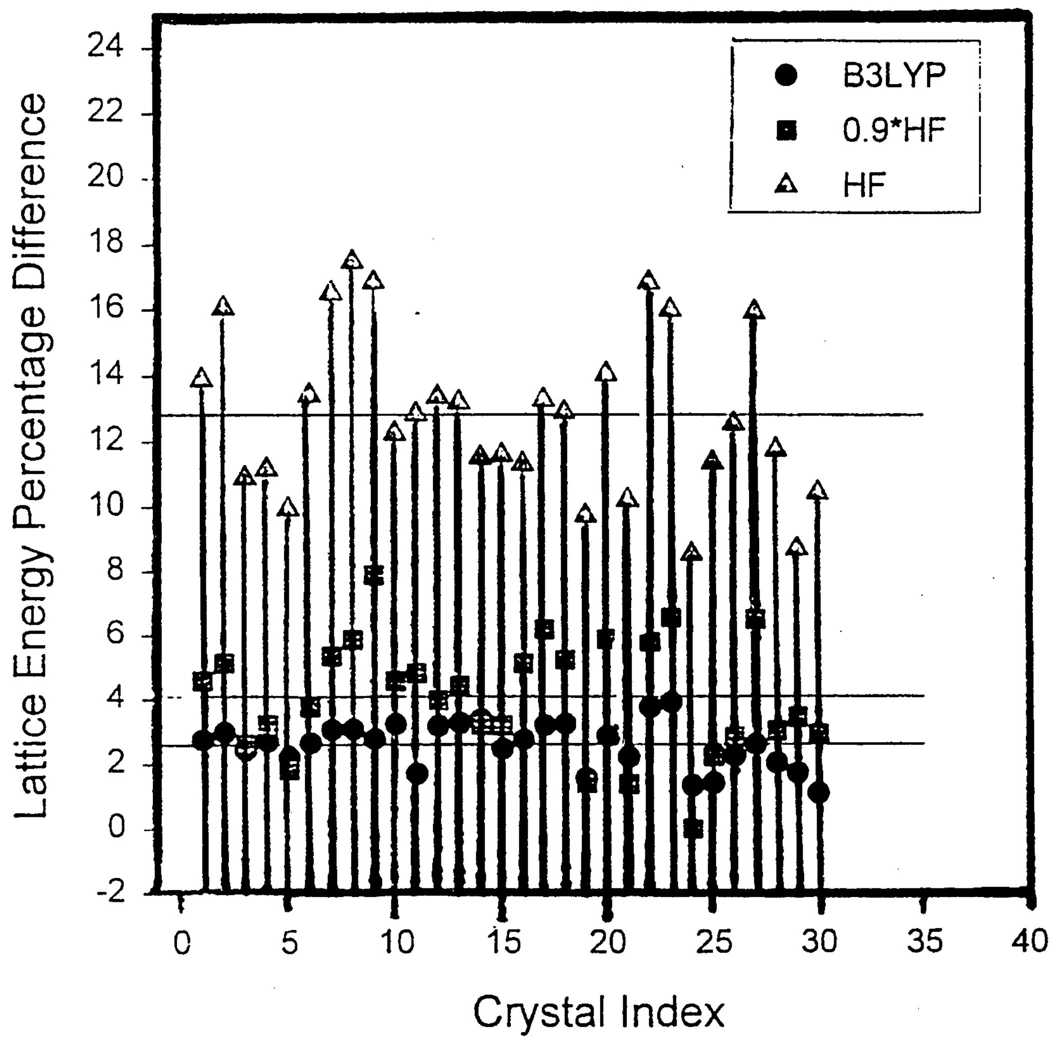


Figure 3. The Percent Differences Between the Lattice Energies and Those Based on the MP2 Values. The Crystal Index Corresponds to the Number of the Crystals in Table 1. The Three Horizontal Lines Indicate the Average Deviations for the Energies Calculated Using the B3LYP (<p1> = 2.6%), 0.9*HF (<p2> = 4.1%) and HF (<p3> = 12.8%) Sets of Charges.

The relative stability of different polymorphic phases of the HMX and HNIW crystals has also been investigated. The calculated MP2 lattice energies for the β, α, and δ phases of HMX are −180.23, −179.15 and −168.24 kJ/mol, respectively. These values support the polymorph stability ranking β > α > δ found experimentally by McCrone [62]. Also, the calculated lattice energies per molecule for the ε-, β-, and γ-HNIW phases of −186.77, −181.29, and −175.31 kJ/mol, respectively, are consistent with the stability ranking ε > β > γ reported by Russell et al. [4].

5. Conclusions

An investigation has been done on the transferability of a 6-exp Buckingham potential previously developed for the α-RDX crystal [1] to 30 crystals, consisting of acyclic, monocyclic, or polycyclic nitramines. The intermolecular potential includes Coulombic interactions between electrostatic charges. These charges were determined from fits to *ab initio* electrostatic potentials calculated for the individual molecules in the experimental configurations.

The tests of this potential for the set of 30 crystals have been performed using molecular packing calculations. Accurate values of the crystal lattice energy have been obtained by employing the accelerated convergence technique for the dispersion and Coulombic lattice sums. Four different electrostatic models, have been considered with charges determined at HF, B3LYP, and MP2 levels, and with charges obtained at HF level uniformly scaled by a factor of 0.9. The predicted geometries indicate a good agreement with the experimental values for the great majority of the crystals in the study. For 90% of the crystals, the structural shift factor was less than 2.0, while for 50% of them, it is less than 1.0.

There is only a small influence, generally below 1%, on the crystallographic parameters by the set of electrostatic charges used. However, the lattice energies are strongly dependent on the electrostatic model. In particular, the best overall agreement with the experimental lattice energies was obtained by using MP2 calculated charges. The lattice energies calculated using the

B3LYP charges overestimate the MP2 energies by about 2.6%, while the overestimation in the case of HF charges is about 12.8%. The procedure of uniformly scaling the HF charges, [10, 25] decreases the differences to about 4.1%. It was also shown that this intermolecular potential correctly describes the order of stability of different phases. The predicted stability $\beta > \alpha > \delta$ is in accord with the experimental findings [62]. Also, the calculated stability ranking $\varepsilon > \beta > \gamma$ for HNIW agrees with the previously reported results [4].

The success of the present potential energy parameters in describing different types of nitramines and different phases at moderate temperatures and low pressure provides incentive to further investigate the transferability of this model to other classes of crystals. Incorporation of intramolecular motion by relaxing the rigid molecular model will also be investigated in future studies.

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We have analyzed the transferability of a previously proposed Buckingham repulsion-dispersion intermolecular potential for the explosive hexahydro-1,3,5-trinitro-1,3,5-s-triazine (RDX) (Sorescu, D. C., B. M. Rice, and D. L. Thompson, *Journal of Physical Chemistry B*, vol. 101, p. 798, 1997) to predict the crystal structures (within the approximation of rigid molecules) of a database of 30 nitramines. These include acyclic, monocyclic, and polycyclic molecules. It is shown that the proposed potential model is able to accurately reproduce the crystallographic structures and lattice energies (where available) of these crystals. For the majority of these crystals, the best agreement with experimental structural and energetic data is obtained in those cases when the electrostatic charges have been determined using *ab initio* methods that include electron correlations effects (namely MP2 and B3LYP). The use of the electrostatic charges calculated at the Hartree-Fock level results in large deviations of the predicted lattice energies from the experimental values. The deviations of the lattice energies can be significantly decreased by scaling the electrostatic charges with a constant factor.

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